

Poly(ethyl methacrylate) and poly(2-ethoxyethyl methacrylate) based polymer gel electrolytes

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Abstract

New poly(ethyl methacrylate) and poly(2-ethoxyethyl methacrylate) gel electrolytes containing immobilised lithium perchlorate solution in propylene carbonate were prepared by UV radical polymerisation. Materials exhibit high ionic conductivity up to 0.23 mS cm^{-1} and long-term stability of chemical and mechanical properties. Both materials keep their suitable conductivity above -20°C . The effect of material composition, temperature, cross-linking agent and salt concentration on the electrochemical and mechanical properties were studied using impedance spectroscopy and cyclic voltammetry. The accessible electrochemical window of both polymer electrolytes was estimated from -2.1 to 1.5 V versus Cd/Cd^{2+} . Impedance measurements showed almost one-order increase of conductivity when ethylene dimethacrylate was used as a cross-linking agent in comparison with the polymer electrolyte without agent.

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1. Introduction

Electrochemical and mechanical properties of polymer gel electrolytes have been intensively investigated since the introduction of the first generation of solid polymer electrolytes by Armand [1,2]. Their electrochemical application includes secondary lithium batteries [1–4], supercapacitors [5,6], and electrochromic devices [7–9]. Wide application of the gel polymer electrolytes is allowed due to the higher ionic conductivity compared with solid polymer electrolytes and due to the higher safety properties in comparison with common liquid electrolytes. Organic acrylate-based polymers are perspective materials for their low toxicity both of monomer and polymer form [10], when methyl methacrylate (MMA) is widely used in the dental praxis. Poly(methyl methacrylate) PMMA

was used in electrochemistry for the first time by Iijima [11] and than either pure [9,12,13] or in different polymer modifications including poly(ethylene-co-methylacrylate) [14], poly(vinylchloride)–PMMA copolymers [15] or poly(glycidyl methacrylate) systems [16]. Aprotic solvents like cyclic carbonates, tetrahydrofuran, *N,N*-dimethylformamide, and formamide are usually incorporated in the gel structure [15–20]. PMMA polymer gel electrolytes with embedded particles of nanosized TiO_2 or Fe_2O_3 [21,22], carbon [23] or proton-conductive membranes with different organic acids [18] and orthophosphoric acid [16] were reported.

Recent polymer gel electrolytes are prepared by immobilisation of an aprotic solvent in the polymer network. Many organic and/or inorganic compounds can be dissolved in the solvent and then uniformly located in the polymer gel medium. There are two general methods of the gel polymer electrolyte preparation. The first method – solvent casting is based on mixture of polymer, salt and aprotic solvent in a volatile co-solvent followed by partial or complete removal of the co-solvent [9,13,24]. The other method

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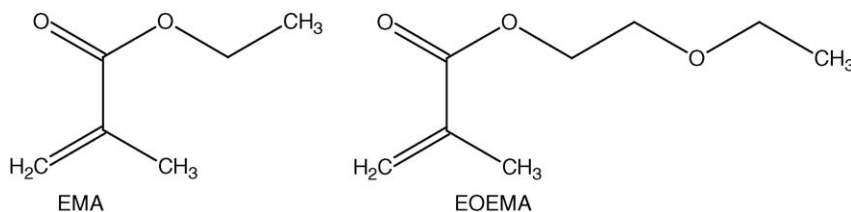


Fig. 1. Formulas of two mainly used monomers EMA and EOEMA.

is in using direct polymerisation of monomers mixed with the aprotic solvent. In this case, thermal or UV polymerisation is used [16,18,25,26]. This method brings the possibility of using cross-linking agent, precise preparation of the gel electrolyte and uniform distribution of compounds previously dissolved in the solvent.

Our previous research was aimed at poly(methyl methacrylate) – propylene carbonate (PC) based electrolytes prepared by the thermal polymerisation of MMA monomer [8,25], when dibenzoylperoxide in oligomeric MMA powder was used as an initiator. Good solubility of various compounds allowed the application of gels in secondary lithium batteries [2,4,27], solid-state gas sensors [28], and electrochromic devices [29]. For detailed description of motion in the structure of polymer electrolytes, gels with ferrocene and other transition metal complexes were prepared and investigated by cyclic voltammetry and impedance spectroscopy and resulted in determination of their electrochemical behaviour in the media without macroscopic liquid phase including estimation of the diffusion coefficients [30].

Generally our research was aimed at two important tasks: the improvement of mechanical stability and increase of the electrical conductivity of materials. This paper brings results of research aimed at acrylate-based polymer gel electrolytes, when several parameters of the preparation were changed with the aim to study the changes of electrochemical and mechanical properties. Electrochemical methods (impedance spectroscopy and cyclic voltammetry) were already used for research of another polymer gel electrolytes [8,25,30]. Defined change of parameters was allowed due to applied UV photoinitiated free-radical polymerisation method of liquid mixture of initial components. The parameters included the carbon chain length of the monomer, type and concentration of the cross-linking agent, concentration of the inorganic perchlorate, and composition of the gel aimed at optimisation of the monomer-protic solvent (propylene carbonate) molar ratio. The main work was done with two different monomers: ethyl methacrylate (EMA) and 2-ethoxyethyl methacrylate (EOEMA; structures are drawn in Fig. 1). The main difference is in polarity of monomers, on the contrary to EMA the 2-ethoxyethyl methacrylate dissolves inorganic salts itself and allows preparation of polymer electrolytes with higher salt content. Our work on this project was based on cooperation between the team of macromolecular chemists and the team of electrochemists, when the feedback between both research teams allowed fluent modification of gel composition and its properties.

2. Experimental

2.1. Materials

Monomeric methyl (MMA), ethyl (EMA), butyl (BUMA), hexyl (HMA), and 2-ethoxyethyl (EOEMA) methacrylate were obtained from Fluka AG. The cross-linking agents ethylene glycol dimethacrylate (1-2, EDMA), diethylene glycol dimethacrylate (2-2), triethylene glycol dimethacrylate (3-2), tetraethylene glycol dimethacrylate (4-2), and hexamethylene dimethacrylate (HexadiMA) were obtained from Fluka AG and Röhm GmbH and their formulas are drawn in Fig. 2. Monomers were distilled before use and stored in the refrigerator at 4 °C. All cross-linking agents and the polymerisation initiator benzoin ethyl ether (Sigma–Aldrich) were used as received and stored in the refrigerator at 4 °C before use. Propylene carbonate (Sigma–Aldrich, anhydrous) was purified by distillation under reduced pressure and stored under molecular sieves. Lithium and sodium perchlorates (Sigma–Aldrich) were dehydrated by vacuum heating at 110 °C overnight and stored in a desiccator.

2.2. Preparation of gel

The polymerisation was carried out in mould formed by polypropylene plate, packing distance frame from silicone rubber and glass plate. The mould, firmly closed using screw clamps was firstly filled by nitrogen and next by monomer mixture, bubbled by nitrogen for 2 min. Initial mixture consisted of monomer, cross-linking agent, solvent (propylene carbonate), lithium or sodium perchlorate and the UV initiator (benzoin ethyl ether). The UV light initiated polymerisation proceeded for a period of 4 h by room temperature using mercury lamp TESLA RVK 125 W (Czech Republic). Obtained samples, the foils with an area 5 cm × 5 cm and thickness corresponded to the thickness of used silicone seals (1.00 ± 0.05 mm), were more or less elastic in dependence of solvent content and mostly transparent. This method of preparation disallows evaporation of the volatile monomer. The composition of the gel is expressed in molar percentage ratio – monomer/PC/salt. The amount of the cross-linking agent is always included in the monomer content. Details of the samples composition and changed parameters are summarised in Table 1.

2.3. Equipment, electrodes and cells

Potentiogalvanostat PGSTAT 10 (Eco Chemie, The Netherlands) was used for electrochemical measurements including

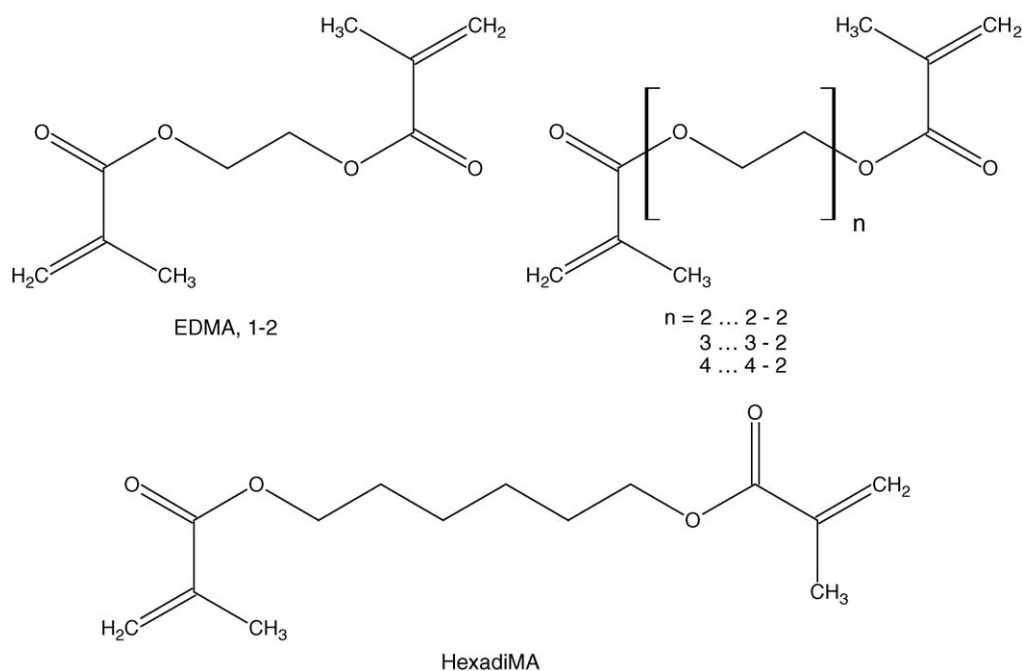


Fig. 2. Formulas and abbreviations of used cross-linking agents (for full names see Section 2.1).

Table 1

Summary of prepared and investigated acrylate-based polymer electrolytes (MA = methyl, ethyl, butyl or hexyl methacrylate)

Changed parameter	Chemical characteristics	Initial composition (mol%)	Cross-linking agent
Monomer type	MA/PC/LiClO ₄	68/30.7/1.3	1 mol% EDMA
Cross-linking agent content	EMA/PC/LiClO ₄	68.4/30.3/1.3	0–2 mol% EDMA
Cross-linking agent type	EMA/PC/LiClO ₄	51.0/45.2/3.9, 60/40/0	0.3 mol%
LiClO ₄ content	EMA/PC/LiClO ₄	53/47/0	0.3 mol% EDMA
Solvent (PC) content in PEOEMA–LiClO ₄ system	EOEMA/PC/LiClO ₄	65.5/0/34.5, 90.5/0/9.5	0.3 mol% HexadiMA

FRA-2 (Frequency Response Analyser) module for impedance measurement. New cell for solid-state electrochemical measurements was developed [30,31] with glassy carbon as the working ($\varnothing = 6.1$ mm) and counter electrodes and PMMA–Cd–Cd²⁺ solid-state reference electrode [25,30,31]. All potentials in the paper are related to this Cd/Cd²⁺ system ($E(\text{Cd}/\text{Cd}^{2+}) = 2.66$ V versus Li/Li⁺). The surface of working and counter electrode was polished by abrasives (0.3 alumina, Metrohm) and soft cloth after each measurement.

Two-electrode arrangement was used for conductivity measurement, when a slide of gel (2 cm × 2 cm) was sandwiched between two parallel stainless steel electrodes. The single potential impedance spectra were measured in the frequency range from 150 kHz to 1 Hz. Obtained spectrum was analysed by the Eco Autolab software producing the values of the equivalent circuit elements. The evaluated value of ohmic resistance was converted in the value of specific resistivity or conductivity. The same procedure was used for the measurement of resistivity in the temperature range from –70 to 70 °C using thermostated bath (precision of the temperature ±1 °C). Except the temperature-dependent measurement, all experiments were performed at 20 °C.

Before and after the voltammetrical measurement a single potential impedance spectrum was measured using the same

three-electrode arrangement with Cd/Cd²⁺ reference electrode, the frequency range was from 100 kHz to 10 Hz and the potential of the working electrode was 0.25 V versus Cd/Cd²⁺, where no electrochemical reaction occurs.

Tensile tests were performed using an Instron 5800 tensile tester at the room temperature and the crosshead speed was 5 mm min^{–1}. Following mechanical characteristics were derived from the stress–strain curves: Young modulus E , tensile strength σ , strain at break ε and energy to break point E_B . Reported values are averages of 10 individual measurements.

3. Results and discussion

3.1. PEMA and PEOEMA based gel electrolytes – influence of the composition on the conductivity and mechanical properties

First experiments were done with different monomers (methyl MMA, ethyl EMA, butyl BUMA and hexyl HMA methacrylate) to study the influence of the side chain length on the mechanical properties and conductivity of prepared gels. The mechanical properties and specific conductivities are summarised in Table 2. The molar ratio of prepared gels was monomer/PC/LiClO₄ = 68.0/30.7/1.3 with the cross-linking

Table 2
Mechanical properties and specific resistivity of gels prepared from different methacrylate monomers; composition monomer/PC/LiClO₄ = 68.0/30.7/1.3 mol% (σ is the tensile strength, ε the strain at break, E the Young modulus, E_B the energy to break point, ρ the specific resistivity at 20 °C)

Monomer	σ (MPa)	ε (%)	E (MPa)	E_B (mJ)	ρ (Ω cm)
MMA	20.0 ± 1.6	4.1 ± 0.9	834 ± 26	284 ± 97	4.1 × 10 ⁵
EMA	1.35 ± 0.18	144 ± 7	1.80 ± 0.21	193 ± 23	4.2 × 10 ⁵
BUMA	0.21 ± 0.01	87.4 ± 4.5	0.74 ± 0.20	19.4 ± 2.2	9.5 × 10 ⁶
HMA	0.33 ± 0.05	116 ± 17	0.59 ± 0.15	35.3 ± 9.1	7.4 × 10 ⁷

agent (EDMA) concentration 1 mol%. Measurements showed low conductivity at the room temperature, especially in the case of butyl and hexyl methacrylate (see Table 2). PMMA based electrolyte was tough and glass-like. With increasing length of the carbon side chain the Young modulus E was rapidly decreasing and the PEMA, PBUMA and PHMA electrolytes were elastic and gelous (see Table 2), when results are corresponding to the polymer theory. Mechanical properties of methyl and ethyl acrylate gels are similar to acrylate-based systems prepared by MacFarlane et al. [32]. No leakage of the liquid component was observed on the samples for the long time period and the materials stored on air keep their elastic properties for several months.

The PMMA based gels prepared by thermal polymerisation were already investigated in our laboratories and were described elsewhere [8,25,30]. Newly prepared gels based on poly(ethyl methacrylate) PEMA showed good mechanical properties, suitable conductivity at the room temperature (see Table 2). Advantages of EMA include lower volatility and higher boiling point (114.5 °C versus 100 °C) in comparison with methylmethacrylate. A set of EMA gels with composition EMA/PC/LiClO₄ = 68.4/30.3/1.3 mol% was prepared with a different concentration of the cross-linking agent (EDMA) from 0.0 to 2.0 mol%. Cross-linkage of the polymer network has a positive influence on the ionic conductivity of prepared samples, when the suitable agent concentration was found 0.3 mol% (see Table 3). However, further increase of the cross-linking agent concentration caused slight increase of the resistivity values. Similar results were obtained in the case of PEMA gels containing 1 or 2 M sodium perchlorate in PC, when the specific resistivity values were fluctuating from 1.5 to 5.2 × 10⁵ Ω cm without clear relationship between the agent concentration and resistivity of material. Generally the non-linked polymer gels exhibited higher resistivity in comparison with moderately cross-linked samples. Cross-linkage of the polymer is common in the macromolecular science and technology [33,34], but only few cross-linked polymer gel electrolytes for electrochemical application

were reported by Arbizzani in PEO–PPO systems [37] and Appetecchi in poly(fluorosilicone)-based systems [35,36]. In both cases improvement of conductivity was observed without further explanation. Our suggested theory is based on fact, that cross-linked polymer is less soluble in aprotic solvents and therefore the immobilised PC liquid phase in the polymer contains lower content of dissolved polymer and exhibits lower viscosity.

While Young modulus and tensile strength are improved by increased cross-linking agent concentration (see Table 3), values of strain at break and energy to breakpoint are decreasing. Polymer electrolytes with low cross-linking agent concentration (under 0.3 mol%) were more viscous and the measurement of mechanical properties did not offer reproducible results. This effect is well-known from the polymer science where the cross-linking agents are widely used to form three-dimensional structure of the polymer network and increasing amount of cross-links leads to improvement of mechanical properties as Young modulus [38–41]. Ethylene dimethacrylate is widely used cross-linking agent in chemistry of polymethacrylates and was employed in our materials from the viewpoint of its hydrophobicity and suitable price [41].

Beside EDMA four other cross-linking agents with increasing carbon chain length and decreasing hydrophobic properties were used for PEMA gels preparation. Specific resistivities of gels with different agents are plotted in Fig. 3, where almost one order decrease or the resistivity was observed due to the incorporation of the cross-linking agent in the structure. The lowest values of resistivity were found in the case of 2-2 and 3-2 agent, but the difference from the gel with 1-2 agent (EDMA) is not significant and would not compensate their disadvantages: higher hydrophilicity and price. Further increase of the carbon chain length of the cross-linking molecule would not improve the conductivity, because the increasing number of the oxygen atoms in the molecule decreases the hydrophobic properties. This effect is unwelcome due to the high hydrophobic properties of EMA and can lead to appearance of non-homogenous

Table 3
Mechanical properties and specific resistivity of poly(ethyl methacrylate) gels containing different concentration of the EDMA cross-linking agent; composition EMA/PC/LiClO₄ = 68.4/30.3/1.3 mol% (variables explained in Table 2)

w (EDMA) (mol%)	σ (MPa)	ε (%)	E (MPa)	E_B (mJ)	ρ (Ω cm)
0.00	–	–	–	–	1.1 × 10 ⁶
0.30	–	–	–	–	1.6 × 10 ⁵
0.50	1.05 ± 0.10	196 ± 15	1.29 ± 0.20	200 ± 22	4.0 × 10 ⁵
1.00	1.35 ± 0.18	144 ± 7	1.80 ± 0.21	193 ± 23	3.4 × 10 ⁵
1.50	1.50 ± 0.18	122 ± 8	1.88 ± 0.29	169 ± 19	3.6 × 10 ⁵
2.00	1.41 ± 0.16	85 ± 7	2.50 ± 0.21	112 ± 18	6.0 × 10 ⁵

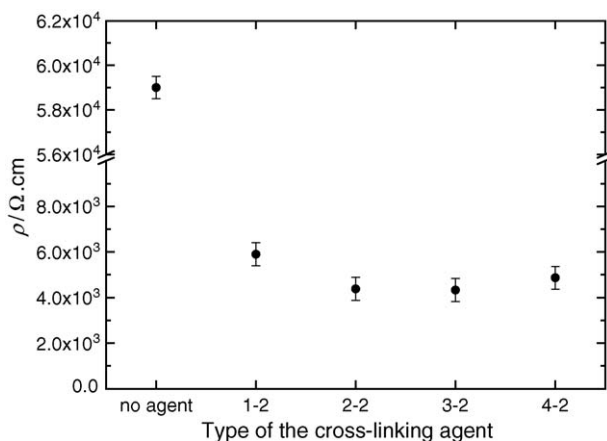


Fig. 3. Dependence of the specific resistivity of PEMA gel electrolytes on the carbon chain length of the cross-linking agent (EMA/PC/LiClO₄ = 51.0/45.2/3.9 mol%; 0.3 mol% cross-linking agent).

domains with different hydrophobicity in the structure. Similar effect was observed by Arbizzani in the PEO–PPO copolymer electrolytes, where presence of the cross-linking agent (butanediol diglycidyl ether) caused an increase of the conductivity [37].

Propylene carbonate is a suitable solvent for inorganic perchlorates and LiClO₄ solution can be prepared with concentration up to 1.25 M. Two sets of PEMA gel electrolytes with different initial monomer/PC ratio were prepared – 60/40 or 53/47 mol%. The content of LiClO₄ increased up to 4.8 mol%. In both cases the impedance measurements showed, that almost three-order decrease of resistivity can be caused by addition of lithium perchlorate solution in comparison to the samples with pure PC only (see Fig. 4). Even low amount of lithium perchlorate in sufficiently high volume of PC (EMA/PC/LiClO₄ = 52.5/46.5/1.0 mol%) exhibits ca. 0.06 mS cm⁻¹ conductivity. The highest specific conductivity, 0.23 mS cm⁻¹ was reached with the gel electrolytes of

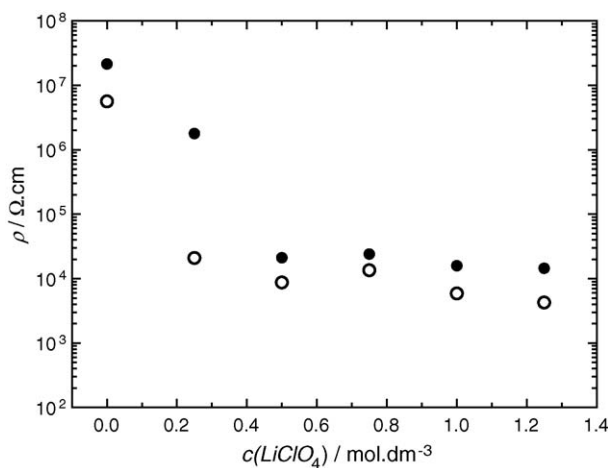


Fig. 4. Dependence of the specific resistivity of PEMA gel electrolytes on the concentration of LiClO₄ in PC. Initial composition was EMA/PC = 60/40 mol% (filled circle) or 53/47 mol% (empty circle); 0.3 mol% EDMA cross-linking agent.

the composition EMA/PC/LiClO₄ = 50.5/44.7/4.8 mol%, when high concentration of the lithium ions is required in the technology of secondary lithium batteries (LiClO₄ concentration in PC is 1.25 M). The increasing association of Li⁺ and ClO₄⁻ ions is caused by increasing salt concentration. Therefore the 4.8-times increase of the salt concentration improves the conductivity 3.8-times only.

Higher content of PC, the only conductive phase in material [26], causes higher conductivity of the PEMA gels. Previously reported PMMA gel electrolytes with 0.5 M LiClO₄ solution exhibited specific conductivity around 0.13 mS cm⁻¹ [25,42–44].

The 2-ethoxyethyl methacrylate monomer was chosen for further synthesis due to its higher polarity caused by higher content of oxygen in the structure. This modification allowed dissolution of LiClO₄ in the monomer itself. PEOEMA containing inorganic salt only exhibited very low conductivity, when the motion of ions is strongly restricted due to the absence of conductive liquid phase. Specific resistivity of the EOEMA/PC/LiClO₄ = 90.5/0/9.5 mol% sample was $2.4 \times 10^6 \Omega \text{ cm}$. This result shows, that the contribution of the polymer phase to the conductivity of material is very low.

Two series of EOEMA gel electrolytes were prepared with the initial composition EOEMA/PC/LiClO₄ = 90.5/0/9.5 and 65.5/0/34.5 mol%, when 3.3–3.4 g mol⁻¹ is the highest accessible concentration of LiClO₄ in the EOEMA monomer. Addition of propylene carbonate to the initial LiClO₄ solution in EOEMA strongly increased the mobility of the ions in prepared gel. Figs. 5 and 6 show significant decrease of the specific resistivity values for both series of prepared samples with increasing volume of PC incorporated in the structure of the polymer. The increase of the conductive liquid phase volume is also connected with decreasing association of the ions and both factors lead to an increase of the material ionic conductivity. Investigation of polyurethane/PC/LiClO₄ electrolytes done by Yoshimoto et al. [45] showed a conductivity maximum at the material composition similar to our samples as plotted in Fig. 5.

On the other hand, when the excess amount of an organic solvent is added to the polymer matrix, the material has not enough strength to keep a solid film. Therefore several mechanical tests were done to find out the suitable material composition. Generally, the PEOEMA gel electrolytes exhibited very good mechanical properties similarly to the PEMA ones.

The lowest resistivity values ($7.4\text{--}7.8 \times 10^3 \Omega \text{ cm}$) for the EOEMA/LiClO₄ = 90.5/9.5 mol% series was reached with the composition EOEMA/PC/LiClO₄ = 58.2/35.7/6.1 and 49.3/45.5/5.2 mol%, where the highest degree of the salt dissociation occurs. Further increase of the PC content caused increase of the material resistivity due to the dilution of the solution (see Fig. 5).

In the case of polymer gels with EOEMA/PC/LiClO₄ = 65.5/0/34.5 mol% composition the minimum resistivity value was not reached due to the limiting composition for the gel formation EOEMA/PC/LiClO₄ = 41.2/37.5/21.3 mol%. This sample with highest content of PC exhibited specific resistivity $4.3 \times 10^3 \Omega \text{ cm}$ at 20 °C (see Fig. 6). Samples with higher solvent content were highly viscous and their mechanical properties

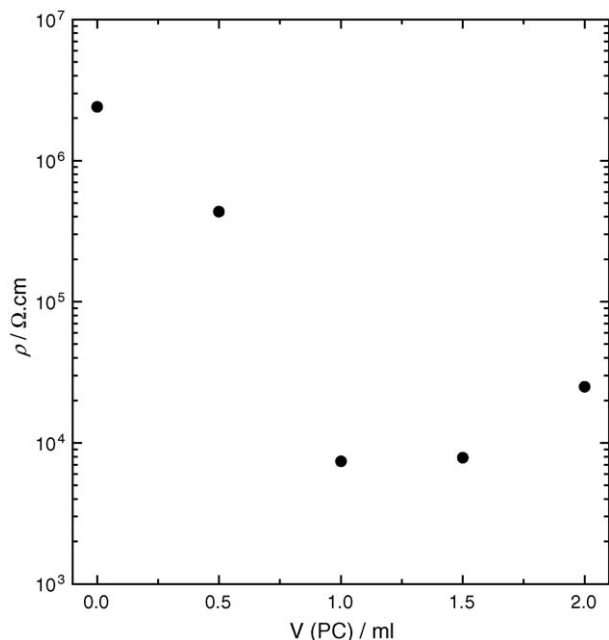


Fig. 5. Dependence of the specific resistivity of PEOEMA gel with LiClO_4 on the amount of added propylene carbonate. Initial composition was $\text{EOEMA/PC/LiClO}_4 = 90.5/0/9.5$ mol%; 0.3 mol% HexadiMA cross-linking agent.

were poor. Theoretically estimated composition of the material with the lowest, ca. $(3.9\text{--}4.0) \times 10^3 \Omega \text{ cm}$ resistivity would be $\text{EOEMA/PC/LiClO}_4 = 37.3/43.1/19.7$ mol%. Unfortunately the higher content of PC than polymer disallows formation of a gel with suitable mechanical properties.

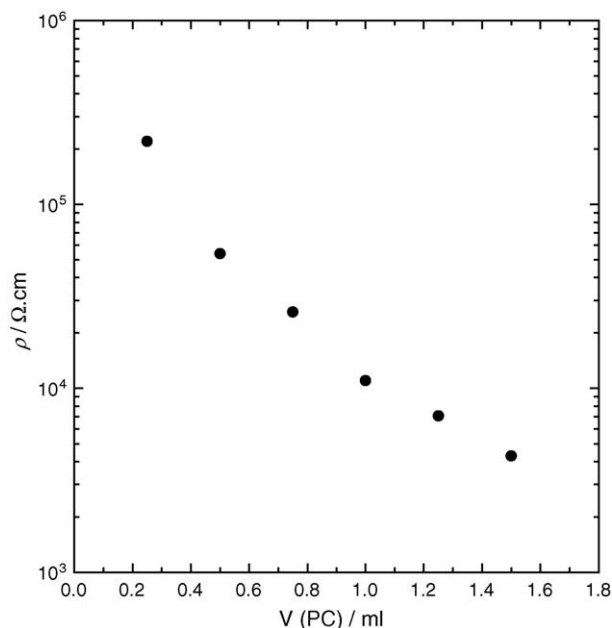


Fig. 6. Dependence of the specific resistivity of PEOEMA gel with LiClO_4 on the amount of added propylene carbonate. Initial composition was $\text{EOEMA/PC/LiClO}_4 = 65.5/0/34.5$ mol%; 0.3 mol% HexadiMA cross-linking agent.

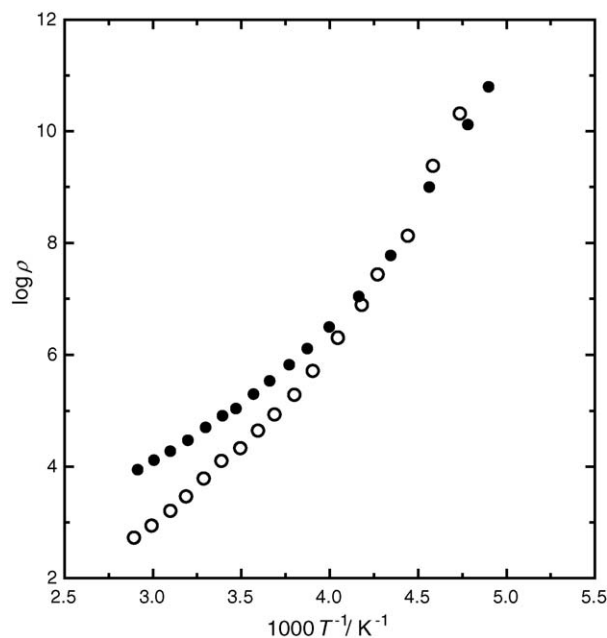


Fig. 7. Arrhenius plot of the specific resistivity vs. reciprocal temperature of PEMA (filled circle) and PEOEMA (empty circle) polymer electrolytes in the temperature range from -70 to $+70^\circ\text{C}$ (composition: $\text{EMA/PC/LiClO}_4 = 58.1/38.6/3.3$ mol%; $\text{EOEMA/PC/LiClO}_4 = 46.7/28.7/24.6$ mol%).

3.2. Influence of the temperature on the electrochemical behaviour of PEMA and PEOEMA gel electrolytes

The influence of temperature in the range from -70 to $+70^\circ\text{C}$ on the specific resistivity of the PEMA gel is plotted in Fig. 7 in the Arrhenius coordinates (specific resistivity is plotted as a decadic logarithm) similarly to our previous work [25,42]. In the case of acrylate-based polymer electrolytes the plot of the specific resistivity consists of two linear parts with different slope. The point of transformation occurs in the temperature range from -25 to -30°C , where the polymer structure is changed from the elastomeric (less organised) to the crystalline form (more organised). This process is associated with remarkable increase of resistivity. At temperatures above 0°C the resistivity values can be expressed by the Arrhenius formula:

$$\log_{10}(\rho) = \frac{A}{T} + B \quad (1)$$

Similarly, the apparent activation energy E_A is accessible from the parameter A using the formula:

$$E_A = 2.303AR \quad (2)$$

Table 3 summarises the room temperature conductivity of methacrylate-based electrolytes including apparent activation energy values and the temperatures of polymer structure transformation. The PEOEMA based samples presents higher conductivity than PEMA gels at temperatures above ca. -25°C (according to $1000/T \approx 4$). Under -25°C both polymer electrolytes exhibit similar conductivity (see Fig. 7).

Impedance spectra of the gel electrolytes measured under various temperatures can be described by two limiting equivalent

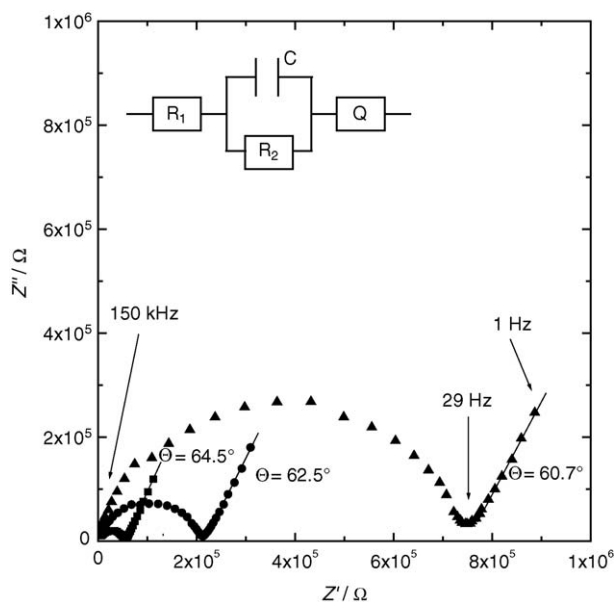


Fig. 8. Nyquist plots of PEOEMA gel measured at -26 (■), -34 (●) and -39 °C (▲) with the corresponding equivalent circuit (composition EOEMA/PC/LiClO₄ = 46.7/28.7/24.6 mol%).

circuits. Nyquist plots for PEOEMA gel are shown in Fig. 8 with the circuit valid for the low temperature region below -20 °C (plotted spectra for temperatures -26 , -34 and -39 °C). The circuit can be described by a formula $R_1(R_2C)Q$ according to the Boucamp notation [46]. The resistances R_1 and R_2 represent contribution of the solidified and immobilised liquid phase to the total resistance. The capacity element C describes dielectric behaviour of the solidified liquid phase and is remarkable only in the low temperature region, where also the viscosity of the PC liquid phase is strongly increasing. At higher temperatures (above 0 °C) the contribution of the capacity element is negligible and the equivalent circuit can be described as the ohmic resistance R in a serial connection with the constant phase element Q (RQ equivalent circuit). Fig. 9 shows Nyquist plots for PEOEMA gel electrolyte measured at 22, 50 and 73 °C. In the temperature region from ca. -20 to 0 °C the behaviour of the polymer gel can be described as transient between the two limiting states. The phase angle is decreasing with the decreasing temperature (see Figs. 8 and 9).

These results are valid for both PEMA and PEOEMA gel electrolytes with respect to different activation energy values caused by distinct polymer structure. Table 4 brings comparison with PMMA gel electrolytes prepared by thermally initiated radical polymerisation of methyl methacrylate monomer and oligomer with PC solution [25,42,44]. The PMMA gel elec-

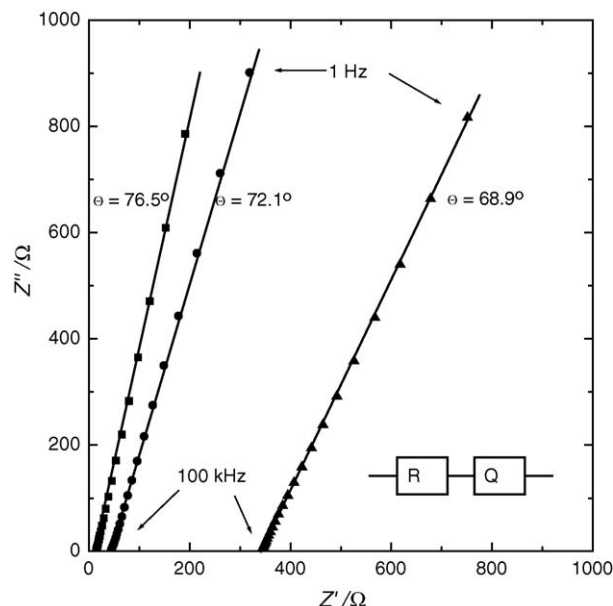


Fig. 9. Nyquist plots of PEOEMA gel measured at 22 (▲), 50 (●) and 73 °C (■) with the corresponding equivalent circuit (composition EOEMA/PC/LiClO₄ = 46.7/28.7/24.6 mol%).

trolytes exhibit higher ionic conductivity at the temperature region under 10 °C and lower activation energy value. This is caused by different structure of the PMMA gel electrolyte in comparison with PEMA and PEOEMA materials, where no oligomer is used and the structure therefore is more uniform and homogenous.

3.3. Cyclic voltammetry of PEMA and PEOEMA gel electrolytes

Our previous investigation of the PMMA gel electrolytes containing lithium perchlorate showed that the accessible potential window is from -0.2 to 1.5 V versus Cd/Cd²⁺ (cit. [42]), although the window of LiClO₄ in pure PC was found wider down to -2.1 V. The limitation of PMMA material is mainly in the area of negative potentials, where several irreversible cathodic waves of oxygen reduction were observed (the origin of oxygen was in PMMA Superacryl[®] powder used for the gel electrolyte preparation) [42]. For the investigation of PEMA and PEOEMA electrolytes the samples with highest conductivity were chosen to minimise the IR drop (sample composition EMA/PC/LiClO₄ = 50.5/44.7/4.8 and EOEMA/PC/LiClO₄ = 41.2/37.5/21.3 mol%).

Initial voltammetry measurements did not show any electrochemical reaction in the potential range from 0.1 to 1.5 V

Table 4

Properties of methacrylate (MA) based gel electrolytes containing LiClO₄ in PC (the symbols ρ , A , B , and E_A are constants from Eqs. (1) and (2))

Polymer	MA/PC/LiClO ₄ ratio (mol%)	ρ (20 °C) (Ω cm)	A (K)	B	E_A (kJ mol ⁻¹)	T_{TRANS} (K)
PEMA	50.5/44.7/4.8	4.4×10^3	2324.7	-6.75	44.5	244.4
PEOEMA	41.2/37.5/21.3	4.3×10^3	3043.0	-6.21	58.3	244.7
PMMA	50.9/46.4/2.7	7.6×10^3	1398.2	-0.89	26.8	243.5

Values for PMMA sample achieved from [44].

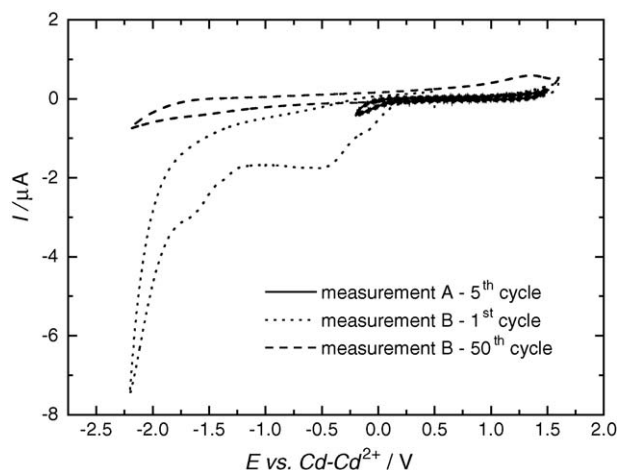


Fig. 10. Cyclic voltammograms of PEMA gel electrolyte (composition EMA/PC/LiClO₄ = 50.5/44.7/4.8 mol%; 5 mV s⁻¹ scan rate).

versus Cd/Cd²⁺ (measurement A on Figs. 10 and 11). The double layer capacity was estimated for PEMA and PEOEMA gel electrolytes 50 ± 5 and $120 \pm 12 \mu\text{F cm}^{-2}$ respectively at the potential 0.25 V, where no electrochemical reaction occurs. No change of conductivity was observed by the impedance measurements before and after each voltammogram, what concludes that no non-conductive layer is electrochemically created by redox reaction of present propylene carbonate, lithium perchlorate or polymer.

The potential limit at the positive side (over 1.5 V) was assigned to the oxidation of propylene carbonate [47,48]. If the potential range was enlarged down to -2.2 V, an irreversible cathodic wave appeared at the potential ca. -0.5 V during the first cycle. Further cycling caused rapid decrease of the wave and it almost disappeared within 3–5 cycles. The voltammograms did not change during the further cycling (measurement B – 50th scan presented in Figs. 10 and 11). This process was already described by Aurbach, when the irreversible wave appearing at the same potential was attributed to the oxygen reduction [47,49]. This wave is greatly reduced in the second and subse-

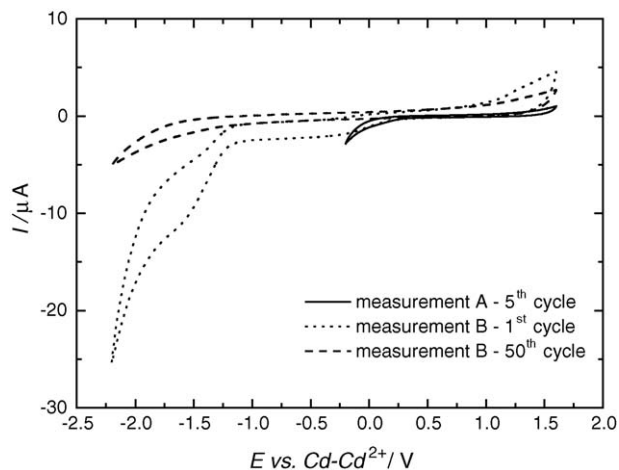


Fig. 11. Cyclic voltammograms of PEOEMA gel electrolyte (composition EOEMA/PC/LiClO₄ = 41.2/37.5/21.3 mol%; 5 mV s⁻¹ scan rate).

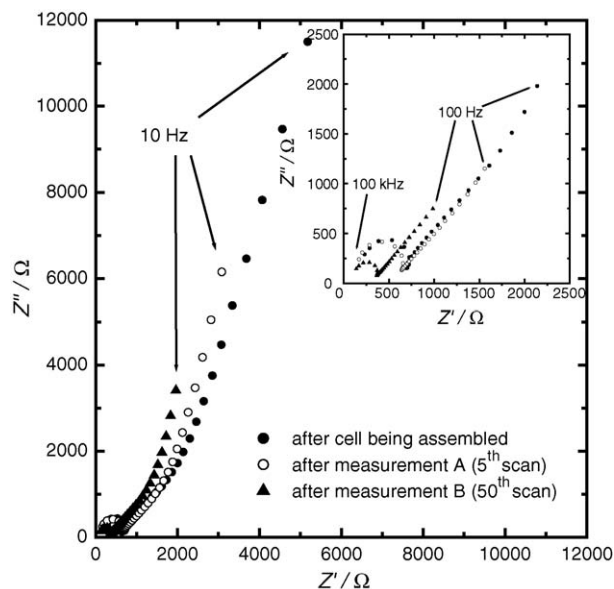


Fig. 12. Single potential impedance spectra measured between the voltammetry measurements of PEOEMA gel (three electrode arrangement, $E = 0.25$ V vs. Cd/Cd²⁺, composition EOEMA/PC/LiClO₄ = 41.2/37.5/21.3 mol%).

quent scans due to the LiO₂ and Li₂O₂ film creation. Formed layer protects the electrode against further oxygen reduction and also suppresses other reduction processes such as water and solvent reduction [47,49,50]. The wave of the irreversible reduction of water was also observed at ca. -1.7 V in both PEMA and PEOEMA gel electrolytes (see Figs. 10 and 11) and the wave was also strongly reduced within 3–5 cycles.

Impedance spectra presented in Fig. 12 show, that no non-conducting layer is formed on the working electrode, when the ohmic resistivity of the material is not significantly changed during the voltammetrical measurements either in narrow or large potential range. This result is consistent with literature [47,50], where the lithium superoxide-oxide layer is conducting and does not passivate the electrode for other electrochemical processes. However, the impedance spectrum measured between the voltammetrical measurement is more complicated to explain in comparison with the spectra measured in Ch. 3.2. The Warburg impedance appearing at higher frequencies proportional to $\omega^{0.44}$ is followed by a constant phase element at lower frequencies (see Fig. 12). During the voltammetrical measurements the double layer capacity increased both for PEMA and PEOEMA samples to the values 190 ± 10 and $500 \pm 25 \mu\text{F cm}^{-2}$, respectively.

4. Conclusions

New poly(ethyl methacrylate) and poly(2-ethoxyethyl methacrylate) gel electrolytes were prepared by UV radical polymerisation and their electrochemical properties were examined. Developed method of preparation allows production of materials with uniform chemical structure and reproducible electrochemical and mechanical properties fulfilling requirements of the technology of lithium-ion batteries and electrochromic devices.

The composition of the material was fluently optimised and the best samples exhibited high ionic conductivity ca. 0.23 mS cm^{-1} at 20°C . The high ionic conductivity was caused by high content of the LiClO_4 solution incorporated in the structure of polymer. The optimisation of the material composition was based on variation of several parameters. Influence of monomer composition, salt concentration, level of the polymer cross-linkage and the salt–solvent ratio on the resistivity of material was investigated. Temperature dependent conductivity measurements showed, that both PEMA and PEOEMA electrolytes exhibit suitable conductivity above -20°C . Prepared samples exhibited suitable and long-term stable mechanical properties.

Voltammetrical measurements showed broad accessible potential window, from -2.1 to 1.5 V versus Cd/Cd^{2+} . No non-conducting layer is formed at low potentials on the glassy carbon–polymer electrolyte interface during the initial voltammetrical measurements, where the waves of oxygen and water traces are eliminated.

In comparison with previously reported PMMA gel electrolytes [25,42] the PEMA and PEOEMA gel electrolytes have higher ionic conductivity above -20°C and broader potential window. Positive influence of the polymer cross-linkage on the conductivity was observed.

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